Année scolaire 2015/2016
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Corrigé de l'exercice 4 - Série 4

Ensemble grand canonique

la fonction de partition est donnée par :

$$Z_G = \mathrm{Tr}\, e^{-\beta(H-\mu N)} \qquad \mu = \text{potentiel chimique}$$

$$= \mathrm{Tr}\, e^{\tilde{\mu} N}\, e^{-\beta H} \quad \text{avec } \tilde{\mu} = \beta\mu$$

$$\Rightarrow Z_G = \sum_{N=0}^{\infty} e^{\tilde{\mu} N} \underbrace{\mathrm{Tr}\, e^{-\beta H}}$$

on a : $\mathrm{Tr}\, e^{-\beta H} = Z(\beta, N)$ est la fonction de partition canonique à la température T fixe (β fixe) et pour le nombre de particules N.

$$\Rightarrow \quad Z_G = \sum_{N=0}^{\infty} e^{\tilde{\mu} N} Z(\beta, N)$$

or la fonction de partition canonique est déjà calculée à l'exercice 3 :

$$Z(\beta, N) = \frac{V^N \left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}}}{N!\ h^{3N}}$$

$$\Rightarrow Z_G = \sum_{N=0}^{\infty} \frac{1}{N!} \left[\frac{e^{\tilde{\mu}} . V \left(\frac{2\pi m}{\beta}\right)^{3/2}}{h^3}\right]^N \ ; \text{ or } \sum_{n=0}^{\infty} \frac{x^n}{n!} = e^x$$

$$\Rightarrow Z_G = \exp\left\{\frac{e^{\tilde{\mu}} . V \left(\frac{2\pi m}{\beta}\right)^{3/2}}{h^3}\right\}$$

$$\Rightarrow \log Z_G = \frac{e^{\tilde{\mu}}\, V \left(\frac{2\pi m}{\beta}\right)^{3/2}}{h^3}$$

a) Energie moyenne : $\langle H\rangle = E = -\left.\frac{\partial \log Z_G}{\partial \beta}\right]_{\tilde{\mu}} = \frac{3 e^{\tilde{\mu}} V}{2 h^3} (2\pi m)^{3/2} \beta^{-5/2}$

b) Nombre moyen de particules :

$$\langle \tilde{N} \rangle = N = \left.\frac{\partial \log Z_G}{\partial \tilde{\mu}}\right]_{\beta} = \frac{e^{\tilde{\mu}} . V \left(\frac{2\pi m}{\beta}\right)^{3/2}}{h^3} = \log Z_G$$

on remarque que $E/N = \frac{3}{2} \frac{\beta^{-5/2}}{\beta^{-3/2}} = \frac{3}{2} \beta^{-1} = \frac{3}{2} kT \Rightarrow \boxed{E = \frac{3}{2} NkT}$

c) fonction de corrélation entre l'énergie et le nombre de particules :

$$G = \langle H\tilde{N}\rangle - \langle H\rangle\langle \tilde{N}\rangle = -\left.\frac{\partial \log Z_G}{\partial\beta\,\partial\tilde{\mu}}\right] = \frac{-\partial}{\partial\beta}\left[\frac{\partial \log Z_G}{\partial \tilde{\mu}}\right] = \frac{-\partial}{\partial\beta}(N)$$

or $N = \log Z_G \Rightarrow G = -\frac{\partial \log Z_G}{\partial\beta} = E = \frac{3}{2} NkT$

d) fluctuations de l'énergie :

$$\langle H^2\rangle - \langle H\rangle^2 = \left.\frac{\partial^2 \log Z_G}{\partial \beta^2}\right]_{\tilde{\mu}} = \frac{-\partial}{\partial\beta}\left[\frac{-\partial \log Z_G}{\partial\beta}\right] = \frac{-\partial E}{\partial\beta} = \frac{3}{2}\frac{N}{\beta^2} = \frac{3}{2}Nk^2T^2.$$

fluctuations du nombre de particules :

$$\langle \hat{N}^2\rangle - \langle \hat{N}\rangle^2 = \frac{\partial^2 \log Z_G}{\partial \tilde{\mu}^2} = \frac{\partial}{\partial\tilde{\mu}}\left(\frac{\partial \log Z_G}{\partial\tilde{\mu}}\right) = \frac{\partial N}{\partial\tilde{\mu}} = \frac{e^{\tilde{\mu}}.V\left(\frac{2\pi m}{\beta}\right)^{3/2}}{h^3} = N$$

e) Chaleur spécifique :

$$C_V = \frac{\partial E}{\partial T} \; ; \; E = \frac{3}{2}NkT \Rightarrow C_V = \frac{3}{2}Nk$$

f) Le grand ~~potentiel~~ potentiel :

$$\Omega = -kT \log Z_G = -kT\, e^{\tilde{\mu}}\frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}$$

$$\Rightarrow \Omega = -e^{\tilde{\mu}}\frac{V}{h^3}(2\pi m)^{3/2}\beta^{-5/2}$$

g) Entropie : $S = k\log Z_G + \frac{E}{T} - \frac{\mu N}{T}$

on a $E = \frac{3}{2}NkT \Rightarrow E/T = \frac{3}{2}Nk$ et on a : $\log Z_G = N$

$$S = Nk + \frac{3}{2}Nk - \frac{\mu N}{T}$$

$$\Rightarrow S = \frac{5}{2}Nk - \frac{\mu N}{T}$$

h) <u>pression</u> :

on a $\Omega = E - TS - \mu N$

$$d\Omega = dE - TdS - SdT - \mu dN - Nd\mu$$

avec $dE = TdS - pdV$

$$\Rightarrow d\Omega = -SdT - pdV - Nd\mu$$

$$\Rightarrow p = \left.\frac{-\partial\Omega}{\partial V}\right)_{T,\mu}$$

$$\Rightarrow p = \frac{e^{\tilde{\mu}}}{h^3}(2\pi m)^{3/2}\beta^{-5/2}$$

on a : $PV = \frac{e^{\tilde{\mu}}.V(2\pi m)^{3/2}\beta^{-5/2}}{h^3} = \underbrace{\frac{e^{\tilde{\mu}}V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}}_{N}\beta^{-1} = NkT$

$\Rightarrow \underline{PV = NkT}$ c'est l'équation d'état du gaz parfait.